

and sintering may be used for applying the metallic bond coating to the substrate. A bond coating of NiCrAlY having a thickness between about 0.003 inches and 0.007 inches has given satisfactory results. The metal bond coating may be a platinum aluminide or diffusion aluminide applied or deposited by CVD or pack cementation as set out, for example, in Bungardt et al., U.S. Patent 3,677,789, which is incorporated herein by reference. A bond coating of platinum aluminide preferably has a thickness of from 0.001 to 0.004 inches.

The thermal barrier coating is preferably a yttria stabilized zirconia. Thermal barrier coatings are set out in Kojima et al., U.S. 4,966,820, issued October 30, 1990, which is incorporated herein by reference. The thermal barrier coating may be applied by thermal spray or electron beam physical vapor deposition (EBPVD). Sputter deposition of yttria stabilized zirconia may be performed using a 10 cm diameter argon ion beam from an electron bombardment ion source of the type developed from electric propulsion technology. Such an ion source is described in "Advanced in Electronics and Electron Physics" by H.R. Kaufman, vol. 36, pages 365-373. Beam extraction may be accomplished by a shielded, two-grid ion optics system. Such a system is described in AIAA Paper No. 76-1017 entitled "A 30 cm Diameter Argon Ion Source". Neutralization of the ion beam can be achieved by using a plasma bridge neutralizer. Suitable thermal barrier coatings include ceramics containing zirconia as a main component and Y_2O_3 (for example, 4 to 20 wt. %), MgO (for example, 4 to 24 wt. %) or CaO (for example, 4 to 8 wt. %) as a minor component. A typical yttria stabilized zirconia contains 6 to 30 weight percent yttria based on the total weight of zirconia and yttria, more preferably 6 to 20 weight percent yttria, and most preferably from 6 to 10 weight percent yttria. The thickness of the thermal barrier layer may be selected from 1 to 1000 microns, and is preferably selected from 50 to 300 microns. Suitable thermal barrier coatings are set out in Strangman et al., U.S. Patent 4,880,514, issued November 14, 1989, which is incorporated herein by reference.

The bond coating comprises a metallic layer of MCrAlY alloy, a continuous adherent alumina layer (formed in situ) on the metallic layer and a discontinuous pure ceramic layer of a particular columnar or lamellar morphology on the alumina layer.

The metallic layer is comprised of a MCrAlY alloy which has a broad composition of 10 to 30% chromium, 5 to 15% aluminum, 0.01 to 1% yttrium (or hafnium lanthanum, cerium and scandium) and M, being the balance, being selected from the group consisting of iron, cobalt, nickel and mixtures thereof. Minor amounts of other elements may also be present. Such alloys are known in the prior art for use alone as a protective coating and are described in various U.S. Pat. Nos. including 3,542,530; 3,676,085; 3,754,903 and 3,928,026 which are incorporated herein by reference. Also suitable is platinum aluminide layers such as disclosed in U.S. Pat-

ent to Bungardt, U.S. 3,677,789, which is incorporated herein by reference.

The thermal barrier coatings are suitable for various metal or ceramic substrates. The thermal barrier coating is preferably applied as an overlay coating to the bond coating which is applied to and overlays a superalloy substrate in any of a variety of applications to nickel-base superalloy substrate based components. One such application is a thermal barrier coating on a jet engine gas turbine blade (10) (component, article) as illustrated in Fig. 1. The substrate of the blade (10) may be formed of any suitable superalloy. One example of such a superalloy is Rene' 80, a well known nickel-base superalloy which has a nominal composition, in weight percent, of 14 percent chromium, 9.5 percent cobalt, 5 percent titanium, 4 percent tungsten, 4 percent molybdenum, 3 percent aluminum, 0.17 percent carbon, 0.06 percent zirconium, 0.015 percent boron, and the balance nickel. Another example is a more advanced nickel-base superalloy such as Rene' N4, having a composition, in weight percent, of 7.5 cobalt, 9.0 chromium, 3.7 aluminum, 4.2 titanium, 1.5 percent molybdenum, 4.0 percent tantalum, 5.0 percent tungsten, 0.5 percent columbium, and balance nickel.

These substrate superalloys are presented as examples, and the coatings are not limited for use with these substrates. A preferred material is Rene NS which is a well known commercially available alloy.

Suitable nickel base superalloys necessarily contain, by weight, 40 to 80% nickel, 5 to 20% chromium, and may contain up to 10% molybdenum, up to 5.5% titanium, up to 6.5% aluminum, up to 3% columbium, up to 9% tantalum, up to 13.5% tungsten, up to 2% hafnium, up to 6% rhenium, up to 20% cobalt, and up to 3% iron. The nickel based alloys may also contain minor amounts of carbon, boron, zirconium, silicon and manganese. They are also likely to contain small amounts of undesirable impurities of sulfur, copper and phosphorus.

Preferred alloys for use as the base of core of composite articles in accordance with this invention are selected from the so-called cobalt base superalloys. These alloys necessarily contain, by weight, 50 to 75% cobalt, 20 to 30% chromium, up to about 10 1/2% nickel, and up to 10% or 11% tungsten. They usually contain small amounts, less than 1% by weight, of carbon, manganese and silicon. They often contain up to about 6% or 7% by weight total of one or more of titanium, boron, silicon, iron, tantalum and columbium. They may also contain small amounts of impurities of sulfur, copper or phosphorus. Specific examples of suitable substrates are set out in Shockley et al., U.S. Patent 3,955,935, which is incorporated herein by reference.

As set out above, the coated article (blade) (10) has (a) a substrate (22), (b) a thermal barrier coating (26) on the substrate (22) and (c) a bonding coat (24) present between the substrate (22) and the thermal barrier coating (26).

As shown in Figure 2, the coated article comprises (a) a superalloy substrate (22), (b) a bond coat (24), (c) an $\alpha-Al_2O_3$ interface layer (28) and (d) a thermal barrier coating (26). Preferably the superalloy substrate has a thickness of >20 mils, the bond coat has a thickness of from 2 to 4 mils, the interface has a thickness of from 0.01 to 0.25 mils, and the thermal barrier coating has a thickness of from 5 to 15 mils.

The adhesion promoting method involves employing one or more of the following steps to form a mature $\alpha-Al_2O_3$ (rhombohedral) scale at the bond coat/TBC interface to enhance adhesion therebetween. The steps are (1) preoxidation; (b) inoculation; (c) surface doping or alloying and (d) noble metals.

1) Preoxidation: The preoxidation of the bond coat should occur before the deposition of the TBC. The preoxidation should occur at temperatures above 1000°C for times greater than 1 Hr. in oxygen rich environments without thermal cycling. Thermal cycling results in the spallation of the bond coat oxide. Reduced pressure environments (vacuum) aren't necessary. There might be an advantage to preoxidation at high total pressure (autoclave). This operation may heal cracks and pores in the bond coat and thermodynamically stabilize the low atomic volume $\alpha-Al_2O_3$ phase.

2) Inoculation: Placing (by slurry, internal oxidation, metallo-organic chemical vapor deposition, EBPVD) a submicron dispersion of oxide particles on the surface could inoculate the bond coat oxide. The submicron oxides would act as nucleation sites thus reducing kinetic barriers to the formation as $\alpha-Al_2O_3$.

Oxides with the same crystal structure of $\alpha-Al_2O_3$ would be most effective and examples are: $\alpha-Al_2O_3$, $\alpha-Fe_2O_3$, Y_2O_3 and Cr_2O_3 .

3) Surface Doping: Elements that oxidize at a faster rate than Al could be added to the surface of the bond coat (such as thin plating, ion implantation, or sputtering) in order to form oxides with the same crystal structure as $\alpha-Al_2O_3$. These elements would include but not be limited to Fe, Cr, and Y.

4) Noble Metals: The reduction in the amount of oxide other than $\alpha-Al_2O_3$ that forms (examples include NiO and Cr_2O_3) would cause a faster transition to $\alpha-Al_2O_3$ formation. Metals that do not form stable solid oxides would accomplish this feat.

These steps improve $\alpha-Al_2O_3$ formation which improves the adhesion of the TBC to the bond coating by avoiding oxide phase transformations.

Claims

1. A method for manufacturing an article (10) suitable for use in a gas turbine engine, said method comprising:

providing a superalloy substrate (22),
applying a metallic bond coating (24) on the substrate,
preoxidizing the bond coating (24) at a temperature above 1000°C for a time greater than 1 hour in an oxygen rich environment,
applying an insulative ceramic thermal barrier coating (26) onto the metallic bond coating (24).

The method of Claim 1 wherein said bond coat (24) is selected from the group consisting of (i) an alumined MCrAlY wherein M is selected from Ni, Co and Fe, (ii) MCrAlY wherein M is selected from Ni, Co and Fe, (iii) a diffusion aluminide and (iv) a platinum modified diffusion aluminide.

The method of Claim 1 or 2 wherein said thermal barrier coating (26) is Y_2O_3 stabilized ZrO_2 .

The method of Claim 1, 2 or 3, wherein said preoxidation occurs at a pressure of greater than 1 atmosphere.

A method for manufacturing an article (10) suitable for use in a gas turbine engine, said method comprising:

providing a superalloy substrate (22)
applying a metallic bond coating (24) on the substrate (22)
inoculating the surface of said bond coat (24) by placing a submicron dispersion of oxide particles on the surface to act as nucleation site

to reduce kinetic barriers to the formation of $\alpha-Al_2O_3$, said oxide particles being selected from $\alpha-Al_2O_3$, $\alpha-Fe_2O_3$, Y_2O_3 and Cr_2O_3 ,
applying an insulative ceramic thermal layer coating (26) onto the metallic bond coating (24).

The method of Claim 5 wherein said particles are placed by applying a slurry of oxide particles to said bond coat surface.

The method of Claim 5 or 6 wherein said bond coat (24) is selected from the group consisting of (i) an alumined MCrAlY wherein M is selected from Ni, Co and Fe, (ii) MCrAlY wherein M is selected from Ni, Co and Fe, (iii) a diffusion aluminide and (iv) a platinum modified diffusion aluminide.

The method of Claim 5, 6 or 7 wherein said thermal barrier coating (24) is Y_2O_3 stabilized ZrO_2 .

A method for manufacturing an article (10) suitable for use in a gas turbine engine, said method comprising:

- providing a superalloy substrate (22),
applying a metallic bond coating (24) on the
substrate (22),
surface coping of the surface of the bond coat-
ing (24) applying elements that oxidize at a fast-
er rate than Al thereto, and elements being se-
lected from Fe, Cr and Y,
applying an insulative ceramic thermal barrier
coating (26) onto the metallic bond coating (24).
- 10 A method for manufacturing an article (10) suitable
for use in a gas turbine engine, said method com-
prising:
providing a superalloy substrate (22),
15 applying a metallic bond coating (24) on the
substrate,
add at least one noble metal to said bond coat
to enhance formation of $\alpha\text{-Al}_2\text{O}_3$,
20 applying an insulative ceramic coating (26) on
to the metallic bond coating.
11. An article suitable for use in a gas turbine engine
comprising
25 a superalloy substrate (22)
a metallic bond coating (24) on the substrate
(22)
a mature oxide scale (28) on the metallic bond
30 coating (24) and
an insulative ceramic thermal barrier coating
(26) on the scale (28) on the metallic bond coat-
ing (24).

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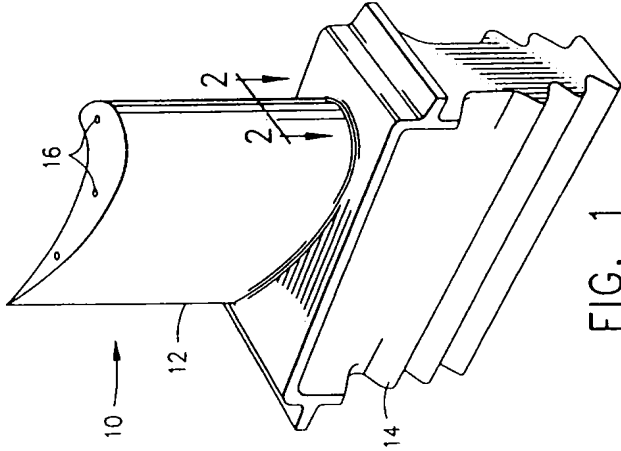


FIG. 1

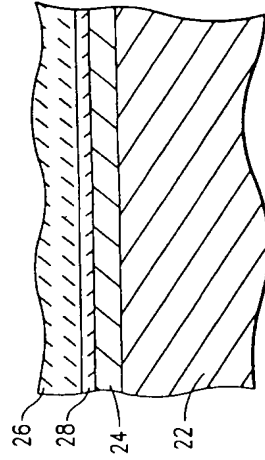


FIG. 2

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European Patent
Office

EUROPEAN SEARCH REPORT

Application number
EP 96 30 9109

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claims	Classification of the application (In C.L.A.)
X	GB 2 159 838 A (UNITED TECHNOLOGIES CORPORATION) * page 2, column 1, line 46 - line 57; * page 2, column 2, line 110 - line 130; claims 1-14 *	1-3, 11	C23C4/02 C23C28/00
X	WO 81 01982 A (UNITED TECHNOLOGIES CORPORATION) * page 8, line 7 - line 23; claims 1-9, 18-21 *	1-3, 9, 11	
X	US 5 238 752 A (EDWARD C. OUDERSTADT) * column 6, line 45 - line 68; claims 1-19 *	1-3, 7-9, 11	
A	US 5 302 465 A (ROBERT A. MILLER) * column 3, line 49 - line 52; claims 1-10 *	1-3, 11	
A	WO 93 18199 A (ROLLS-ROYCE) * claims 1, 16, 20 *	1-3, 11	TECHNICAL FIELD SEARCHED (In C.L.A.)
A	EP 0 236 520 A (HITACHI) * claims 1-11 *	1-3, 11	C23C
A	EP 0 340 791 A (HITACHI) * page 7, line 42 - line 51; claims 1-11 *	1-3, 11	
A	EP 0 567 252 A (GENERAL ELECTRIC COMPANY) * page 3, column 4, line 37 - line 59; claims 1-20 *	1-3, 11	
P, X	EP 0 733 723 A (HOMMET CORPORATION) * claims 1-17 *	1-3, 7, 8, 11	
The present search report has been drawn up for all claims			
Name of inventor		Date of submission of the search	Examiner
THE HAGUE		20 March 1997	Elsen, D
CATEGORY OF CITED DOCUMENTS X: priority or principle underlying the invention Y: particularly relevant if taken alone V: particularly relevant if combined with another document of the same category A: document of the same category O: non-written document P: intermediate document 1: filing or principle underlying the invention 2: filing or principle underlying the invention after the filing date D: document cited in the application 1: document cited for other reasons 2: document cited for other reasons 3: number of this same patent family, corresponding document			

EP 0 780 484 A1 (PCT/EP 96/001)